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Real-Time Intelligent Chemical and Biological Nanosensors on Flexible Platform

by Govind Mallick, Shashi P. Karna, and Pulickel M. Ajayan

ARL-TN-325 **July 2008**

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14. ABSTRACT
As a first step toward realizing real-time nanoscale electronic sensors for chemical and biological agents, we have successfully fabricated arrays of switching elements in open-channel configurations using single-walled carbon nanotubes (SWNTs) as the carrier transport medium. Using a chemical-vapor deposition process, we have grown long strands of SWNT bundles and used them to fabricate multiple arrays of switching devices with the channel length of 3, 5, 7, and 10 μm on a 15- × 15-mm SiO2-on-Si substrate. Regardless of the channel length, a large majority of the fabricated devices show current rectification characteristics, with a very high throughput of current in the forward bias. The exact physical mechanism of the observed current rectification could not be established. However, the atomic force microscopic analysis of the device structure and morphology of the SWNT suggest the observed rectification to result either from cross-tube junctions or a mixture of metallic and semiconducting tubes in the SWNT bundles.

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nanotechnology, nanoscale applications, nano-materials, rectification, chemical vapor deposition, single-wall CNT

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1. Background

There is a critical need to develop enhanced soldier protection against chemical and biological warfare agents in full spectrum operation and soldier protection in counter-insurgency environment. There is a need to detect, identify, and neutralize chemical, biological, radiological or nuclear (CBRN) threats as identified in the Future Force (FF) and Current Force (CF) Capability Gaps (FF1, FF3, FF6, CF4, CF7). There is also a critical need to detect explosive hazards such as improvised explosive devices (IEDs) and mines before they can affect the soldier or system's ability to maintain momentum of the maneuver forces and the ability to detect IEDs and mines from safe stand-off distance (FF1, FF3, FF6, CF4, CF5, CF6, CF7). Current systems to address these needs are too bulky, take longer (several minutes) detection times, and often unsuitable for dismounted soldier application.

Some of these capability gaps can be addressed by exploiting novel properties of nanoscale materials, whose dimension and collective functionalities offer unique opportunity to develop ultra-light weight, low-power consumption, real-time sensing, processing, and communication systems. For example, recent breakthroughs in the experimental measurements of single-molecule conductance (*1*), negative differential resistance and other electrical properties (*2*) demonstrate the potential of developing molecular-level electronic sensing elements. Similarly, recent experiments, demonstrating the feasibility of massively parallel, high-throughput field-effect transistors fabricated from single-walled (SW) carbon nanotube (NT) as the current switching medium (*3*) and room-temperature operational single-electron transistors (SETs) fabricated from focused-ion beam (FIB) evaporated metal quantum dots (QDs) (*4*) strongly suggest the possibilities of developing electronic sensing and processing devices utilizing novel properties of molecular and nanoscale materials. When realized, such devices would demonstrate molecular-level sensitivity, extremely high-degree of specificity, order of magnitude reduced weight compared to current systems, and extremely low-power operation.

However, several critical challenges remain in realizing technologically viable nanoscale sensing and processing devices combining the chemical recognition properties of molecular materials with the electronic properties of nanoscale materials. The biggest challenge associated with realizing molecularly recognizable electronic sensors is the integration of dissimilar materials at nano and micro scales without loosing their individual unique properties. Another challenge is the material incompatibility of organic molecules with Si and other solid state devices, which prevents their integration directly in microelectronics devices.

In order to address these issues, here we present a novel approach for developing molecular-nanoelectronics that promises to the opportunity to realize real-time nanoscale electronic sensor-processor system for detecting chemical and biological species. Our approach is based on utilizing the unique electrical properties of chemical vapor deposited (CVD) single-walled

carbon nanotube (SWNT) metallic wires and transistors for conductive/resistive detection of chemical species.

2. Objectives

The objectives of this research are to examine the feasibility of real-time sensing of chemical and biological species by utilizing the unique materials and electronic properties of carbon nanotubes and demonstrate, when possible, the multi-agent sensing and information processing capabilities of such devices. The specific goals of the present research are to (a) understand and develop process flow for SWNT growth with desired electronic properties, (b) fabricate electronic devices utilizing the SWNTs and characterize their electrical properties, and (c) demonstrate single and possibly multiple chemical agent sensing and detection properties of SWNT nanoelectronic devices.

3. Approach

The approach taken to realize the objectives consists of three distinct parts: (1) process optimization for the growth of switchable SWNT on technologically compatible substrates, (2) fabrication and electrical characterization of SWNT switching devices, and (3) chemical agent sensing and detection with the use of fabricated SWNT electronic devices. In the first year of the proposed research, we accomplished the fabrication of functional switching devices, thus completing the first two parts. The third part, the sensing and detection of chemical species is underway and its results will be presented in the next report.

4. Experiments

4.1 SWNT Growth and Characterization

SWNTs were grown in Ajayan's Lab at the Rensselaer Polytechnic Institute (RPI) using metal nanoparticle catalyzed CVD process. Specifically, methane (CH_4) gas was used as the feedstock for carbon source. Fe-nanoparticles were used as the catalyst for carbon nanotube (CNT) growth. A Fe-nanoparticle coated 100-nm-thick silicon oxide layer on heavily-doped silicon was used as the substrate. The catalyst nanoparticle coated substrate was placed inside the tube oven and heated to 920 °C under a constant argon flow (~50 sccm) and pressure of 500 Torr. Upon reaching the set-point temperature, the system was maintained at these conditions for 10 min to

ensure that the environment inside the tube furnace was stable. Finally, the argon flow was turned off and the methane flow was simultaneously initiated at a rate of ~100 sccm. After 5 min, the growth was ceased by turning off the methane flow, evacuating the system to 200 mTorr and allowing the system to cool to room temperature over a period of 2.5 hr. This CVD technique coupled with novel catalyst system allowed relative control of the nanotube properties such that the final product could be easily converted into a working device.

4.2 Surface Characterization

Surface characterizations of the as grown SWNT samples were performed by atomic force microscopy (AFM: CP-II, Veeco). The post-fabricated devices were analyzed by scanning electron microscope (SEM: Hitachi S-4700) to investigate the structure of the devices and the gaps between the electrodes (source and drain) while AFM was used to locate the bridging carbon nanotubes between the electrodes under ambient conditions.

4.3 Device Assembly and Processing

The SWNT-FET devices were fabricated by depositing 100 nm layer of Au on a 10-nm thick Ti that served as source (S) and drain (D). A single substrate (chip) with an approximate size of 15×15 mm comfortably housed about 135 devices. These included four different types with a channel length (gap) between the electrodes (S and D) of 3, 5, 7, and 10 μm, respectively.

4.4 Electrical Characterization

The electrical properties of the assembled MFET devices were examined by I – V measurements using the semiconductor (SC) analyzer system (Janis/Keithley-4200; Micro Manipulated Cryogenic Probe System). Some of the devices, specifically those near the edges of the substrate were damaged and could not be probed. Of the 135 fabricated devices, 103 devices were probed, of which 35% (36 out of 103 devices) of the devices were found to be active in this particular sample. Out of these active devices, 61% of 3-μm gap, 28% of 5-μm gap, 22% of 7-μm gap, and 26% of 10-μm gap devices were found active, i.e., they showed measurable electrical characteristics. Out of the active devices, most of them (72%) showed asymmetric I-V curves and rest of them were metallic.

5. Results and Discussion

Figure 1 shows the AFM image and height profile of as grown raw SWNTs on a 10- × 10-μm Si/SiO_2 substrate. As indicated by the height profile, the SWNTs were 2–3 nm in height but almost 100 nm in thickness. In general, individual SWNTs are 2–3 nm in diameter. Atomic resolution image of part of the nanotube shown in figure 2 revealed that each strand of

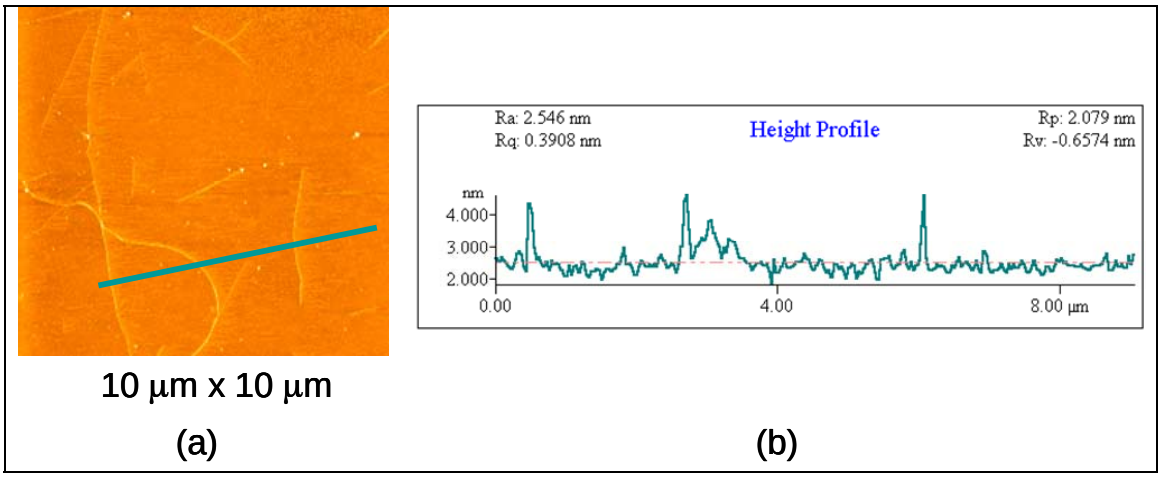

Figure 1. AFM image of CVD grown SWNTs (a) and the related height profile (b).

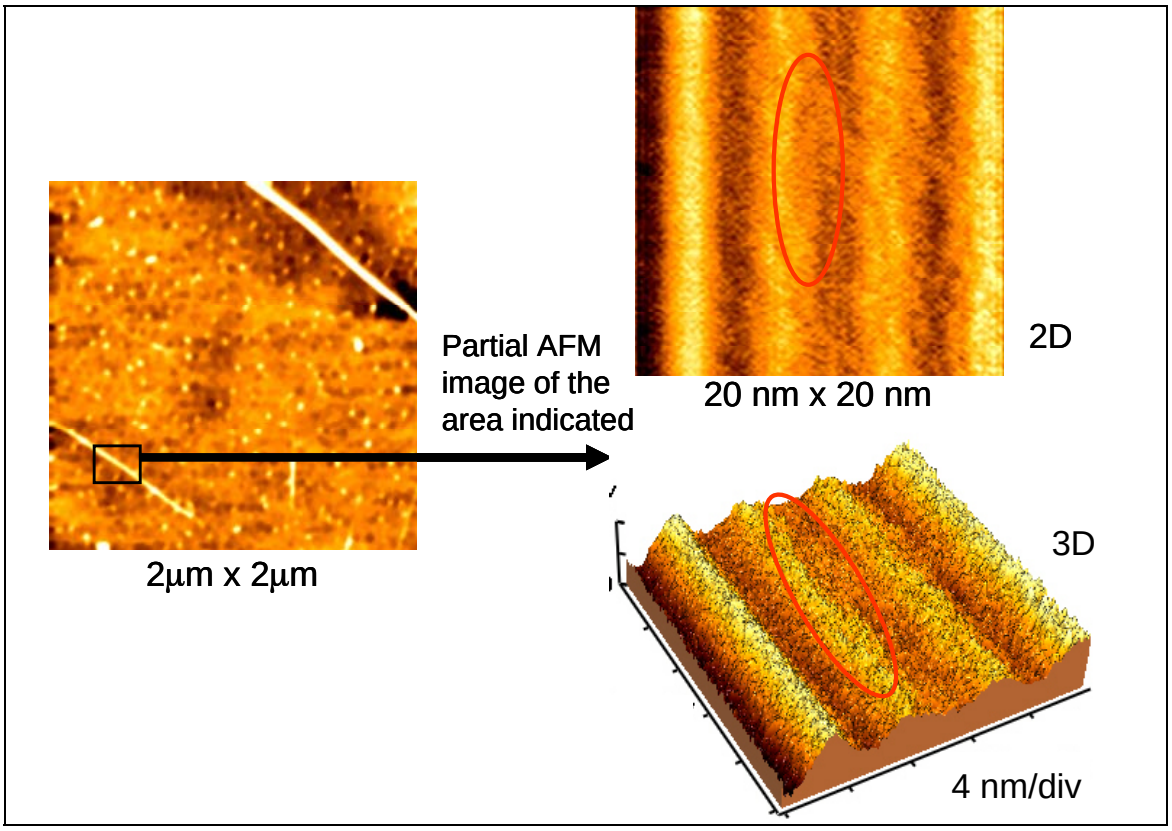

Figure 2. Partial atomic resolution AFM image of the area indicated. The highlighted area (in red) shows possible defects in CNT.

nanotube shown in figure 1 was, in fact, a bundle of several single nanotubes aligned parallel to each other. For one segment of a nanotube bundle, the AFM scan shown in figure 2 exhibit four individual nanotubes aligned parallel to each other, with individual diameter of about ~2 nm each in a scan area of 20 × 20 nm.

The SEM images of fabricated devices are shown figure 3. Each device was uniquely labeled (shown in the inset as matrix of figure 3a) for easy access. The appropriate dimension of each device is also indicated in figure 3b. Figure 3c shows an AFM image of a linear bundle of SWNTs connecting the 10-µm gap electrode pads. We were able to locate SWNTs wire connecting the pads with all four gap devices.

Typical I-V characteristics of device number 7 14-11 are shown in figure 4 which shows diode like behavior. There are a number of possible reasons, such as the X- and Y-type junctions, mixture of metallic and semiconducting tubes in nanotube bundles giving rise to Schottky-type junctions, similar junctions at the electrode-nanotube contacts, and internal structural defects in individual tubes. In the case of the shown 7-µm gap device, the AFM image clearly shows X and Y-type junctions in the SWNT bundle connecting the two electrode pads. The drain current for the control sample (inset, lower-right corner) on the same scale is negligible (pA). As has been also observed earlier (*1*), the noted rectification in this particular device could very well result from the nanotube junction formation. On the other hand, we also observe rectification behavior in the electrical properties of the device when the Au electrodes are bridged by straight bundles of SWNTs (inset, upper-left corner), as shown in figure 5 for a 10-µm gap device. The inset of figure 5 shows the I-V characteristics of a control device with nearly negligible current due to the absence of the SWNT in the channel.

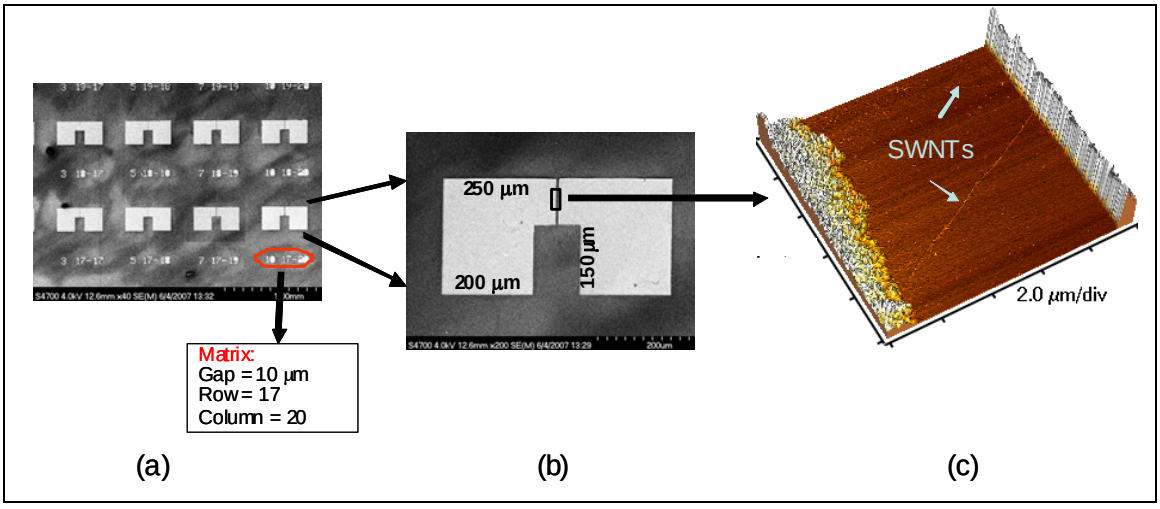

Figure 3. SEM images of different device patterns (a), exposed view of 10-µm gap device (b), and 3-D AFM image of 10- × 10-µm area of the device showing SWNTs connecting the two electrode pads (c).

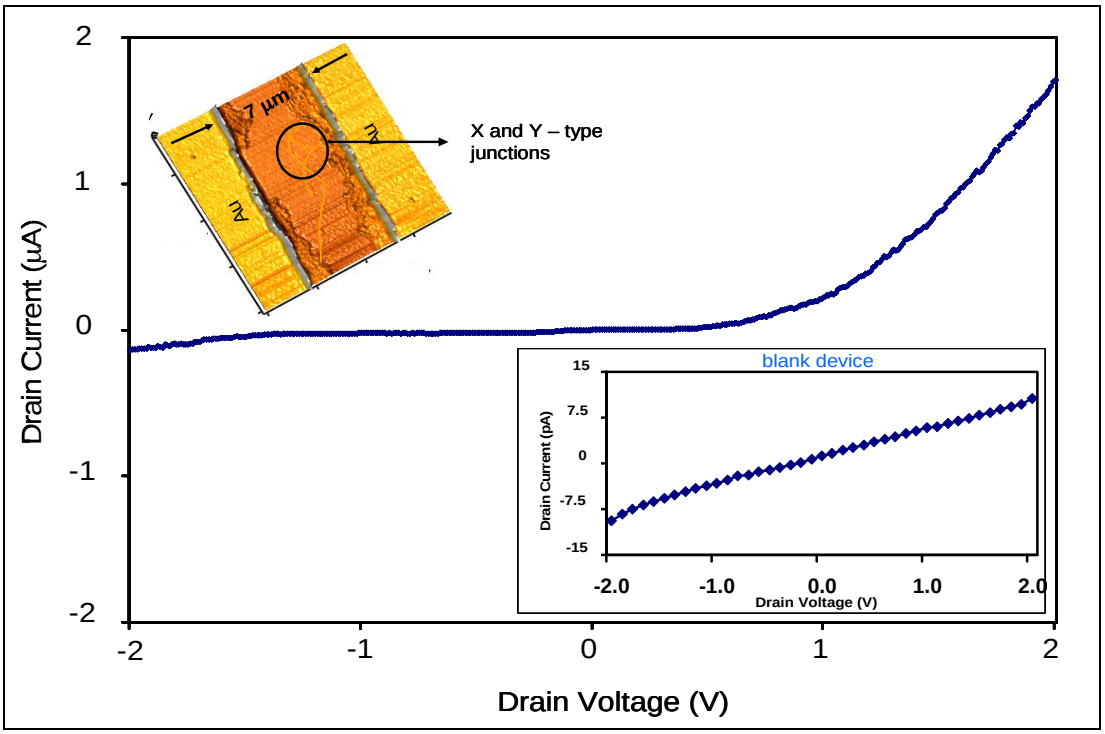

Figure 4. Two terminal-V measurements of 7-μm gap device (device no. 7 14-11). The I-V of a blank device of same gap size is shown in the inset.

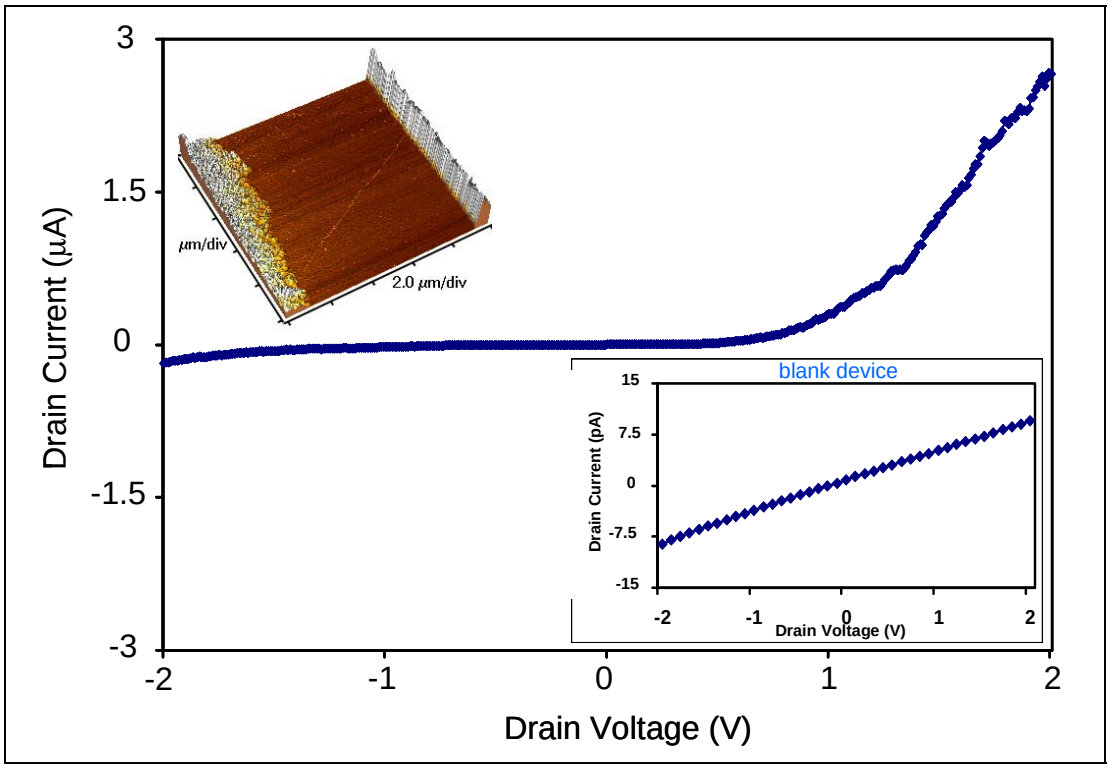

Figure 5. Two terminal I-V measurements of 10-μm gap device (device no. 10 13-12). The I-V of a blank device of the same gap size is shown in the inset.

Rectification (or diode) like behavior in I-V characteristics of a p/n type device, is due to the shift of electrons to opposite junctions that causes big energy barrier to prevent the electron flow to reverse direction. There have been several reports of CNTs showing diode like behavior in the past (*1–2*, *5–7*). These observations have been attributed to the geometrical or atomic-level changes in the structure of the tubes. For example, the Y-junction CNTs generated from pyrolysis method (*1*) have shown distinct diode properties when probed on the Y-junction. But, they show symmetric I-V curves when measured on the uniform part of the nanotube. Several others have shown diode like behavior in CNTs by modifying the tube, either by doping them with p/n type dopants (*5–6*) or by creating a p-n junction by using split gate (*7*). In general, rectification in nanotubes is caused by creating an energy barrier at the junction by the change in the internal structure of the tube. However, this type of behavior is seldom seen in as-grown CVD-deposited CNTs. Typically, CVD-grown SWNTs show either a metallic or semi-conductive behavior (*3*). Here, we report asymmetric behavior in the I-V characteristics of CVD grown SWNTs, possibly due to the internal defect, as shown in the atomic resolution image of SWNT bundle in figure 2. However, additional investigations are needed to clearly identify the underlying physical mechanism of the observed diode-like behavior.

The current and its voltage derivative (conductance) as a function of applied voltage dominant diode type SWNT devices fabricated in this study are summarized in figures 6a and b, respectively. It is clearly seen that the magnitude of the drain current is significantly higher at the positive bias compared to the negative bias indicating a pure diode property of the devices. The open device architecture used in the present work has led us to explore the new regime and properties of SWNTs. It is anticipated that the present research would open new application areas for SWNT-based electronics. For example, the rectification properties and high throughput of the fabricated device could be utilized for DC to AC conversion in high-power electronics. Experiments demonstrating such applications are underway and will be presented in the second year report.

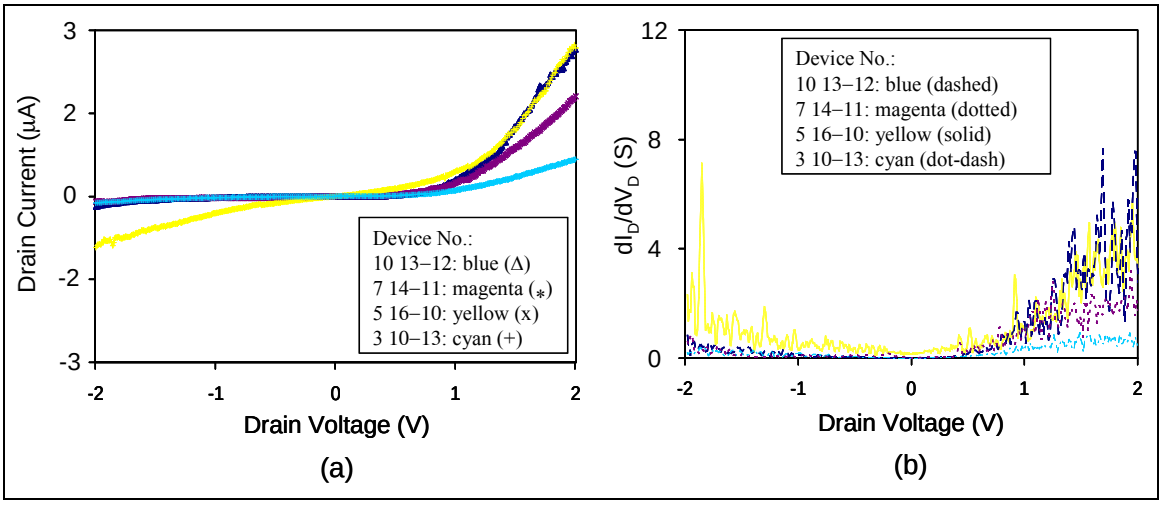

Figure 6. Two terminal I-V measurement of four different gap devices (a) and their respective conductance plot (b).

6. Conclusions

We have grown SWNT by CVD process and fabricated arrays of SWNT electronic switches in open channel configurations. A large majority of the devices fabricated with the as-grown SWNT exhibit prominent rectification characteristics.

We have also demonstrated the fabrication of massively patterned SWNTs switching devices on a single chip. The process is compatible with the current industry-standard Si-electronics and could be easily transitioned for mass fabrication of the SWNT switching devices. The open-device architecture also offers the opportunity of utilizing the SWNTs as chemical and biological sensors. Additionally, a large number of FETs on a single chip would potentially allow us to develop multiagent sensors. Research exploring the possibility of such sensors is currently underway in our laboratory.

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